

Novel Non-Precious Metals for PEMFC: Catalyst Selection through Molecular Modeling and Durability Studies

Branko N. Popov, Vijayadurga Nallathambi, Gang Wu,
Xuguang Li, Sehkyu Park, Lingyun Liu, Swami Kumaraguru,
Hector Colon-Mercardo, Nalini Subramanian, Jong-Won Lee

University of South Carolina

May 15, 2007

Project ID: FC5

Project Overview

Timeline

- Project Start Date - 9/30/2003
- Project End Date - 9/30/2007
- Percent Complete - 90%

Budget

- Total Project Funding
 - DOE Share- \$ 1,376,292
 - Contractor Share - \$351,207
- FY 03 - \$ 200,000
- FY 04 - \$ 125,000
- FY 05 - \$ 400,000
- FY 06 - \$ 525,000
- **FY 07 - \$ 126,292**

Technical Barriers and Targets

- **Electrode performance**
Perform at least as well as the conventional Pt catalysts currently in use in MEAs
- **Durability**
2,000 hours operation with less than 10% power degradation
- **Material Cost**
Cost at least 50% less as compared to a target of 0.2 g of Pt / peak kW

Partners / Collaborations

- **Case Western Reserve University**
 - Molecular Modeling
- **Northeastern University**
 - Structural Studies



Project Objective

OVERALL:

To develop non-precious catalysts for PEMFC with high catalytic activity, selectivity and durability which perform as well as conventional Pt catalysts with a cost at least 50% less than a target of 0.2 g (Pt loading) / peak kW

SPECIFIC FOCUS:

2003 - 2004

Transition metal-chelate catalysts

- Catalyst screening
 - Mo-Ru-Se/C, Ru-N/C, Ru-Fe-N/C, Co-N/C, Fe-N/C, Cr-N/C, Cu-N/C, Ni-N/C
- Specific focus
 - Ru-N/C, Ru-Fe-N/C, Co-N/C

2005

Carbon-based metal-free catalysts

- Surface modification of porous carbon with:
 - (i) oxygen functional group
 - (ii) nitrogen functional group
 - (iii) non-metallic additive "X"

2006 - 2007

Carbon composite catalysts

- Use of metal-free catalysts as a catalyst support
- "Metal-catalyzed pyrolysis" to increase the number of active sites
- Chemical post-treatment



Technical Accomplishments

- ❑ Highly active carbon-based metal-free catalysts were developed.
 - ❑ Carbon activation methodology was developed to synthesize metal-free catalyst with surface functional groups.
 - ❑ Onset potential as high as 0.82 V vs. SHE was obtained.
 - ❑ No H₂O₂ generation (FOUR electron pathway for ORR).

- ❑ Highly active carbon composite catalysts were developed.
 - ❑ Metal-free catalyst was used as a catalyst support to increase the activity and selectivity.
 - ❑ Metal-catalyzed pyrolysis process was developed to increase the concentration of active sites and the stability.
 - ❑ The post-heat-treatment and chemical treatment were optimized.
 - ❑ FOUR electron pathway for ORR.
 - ❑ No catalyst degradation in fuel cell for 80 h of continuous operation.



Initial Work at USC (FY 2003 - 2004)

Approach:

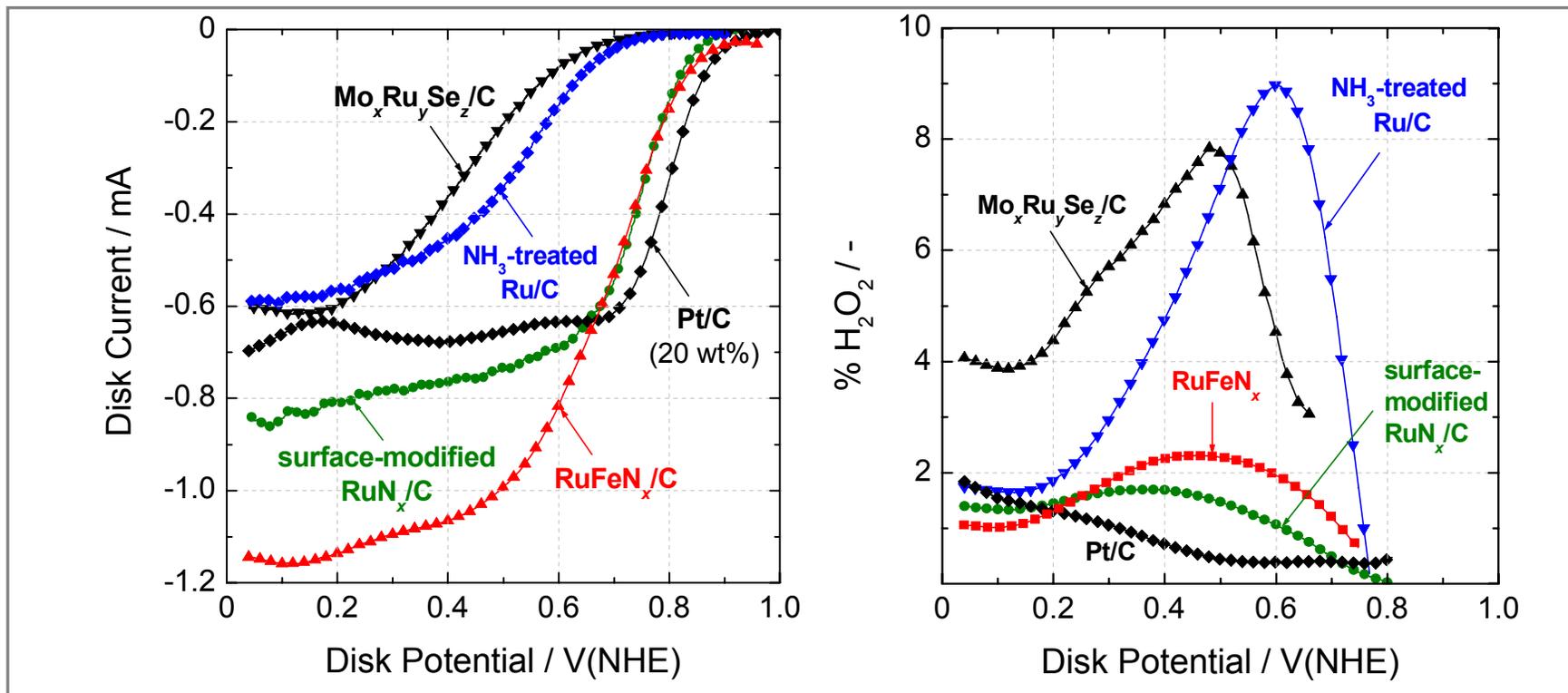
To develop transition metal (Ru, Co, Cr, Fe, Ni, Cu, etc.) based chelate catalysts using activated carbon, surface modifier and non-metallic additive

- ❑ The active reaction sites for ORR were optimized as a function of:
 - ❑ concentration of surface oxygen groups
 - ❑ concentration of surface nitrogen groups
 - ❑ non-metallic additive
 - ❑ carbon support (porosity and pore size distribution)
 - ❑ metal loading
 - ❑ surface modifier
 - ❑ pyrolysis temperature

The synthesis methodology developed at USC offers flexibility to easily control the catalyst composition and thus to increase the concentration of active reaction sites.



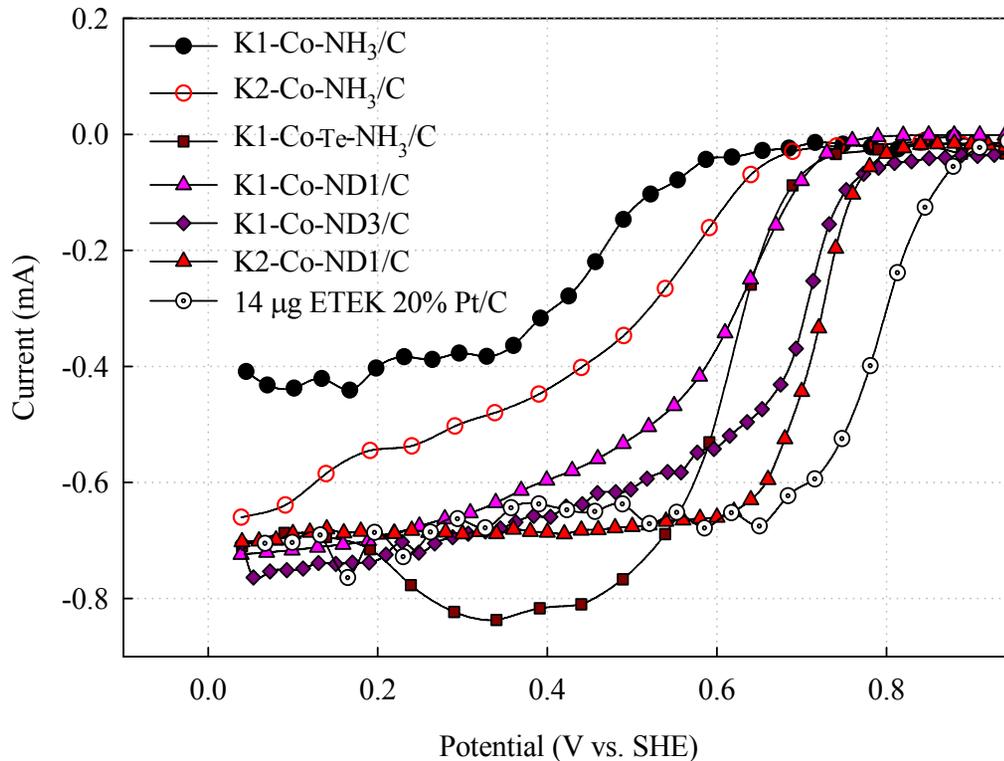
Ru-Based Catalysts



- **HIGHLIGHT:** The surface-modified Ru-N/C catalyst shows comparable catalytic activity and selectivity to the Pt/C catalyst.
- The Ru-N/C catalyst generates less than 2% H₂O₂ during oxygen reduction.



Co-Based Catalysts

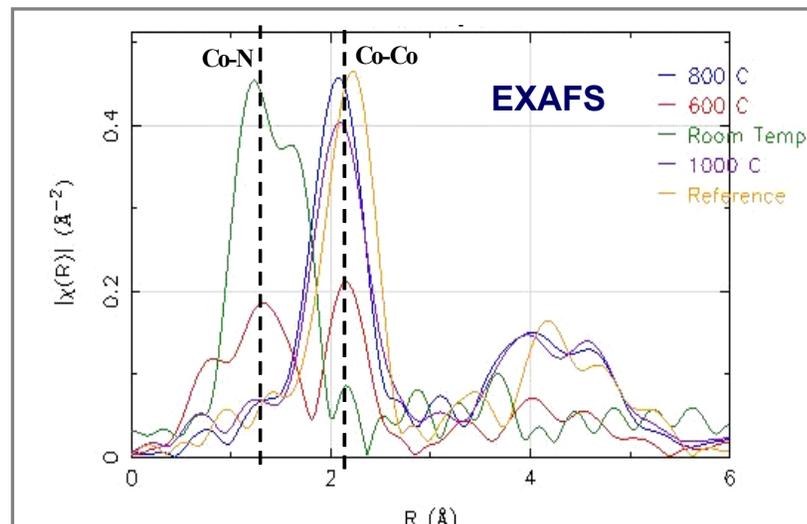
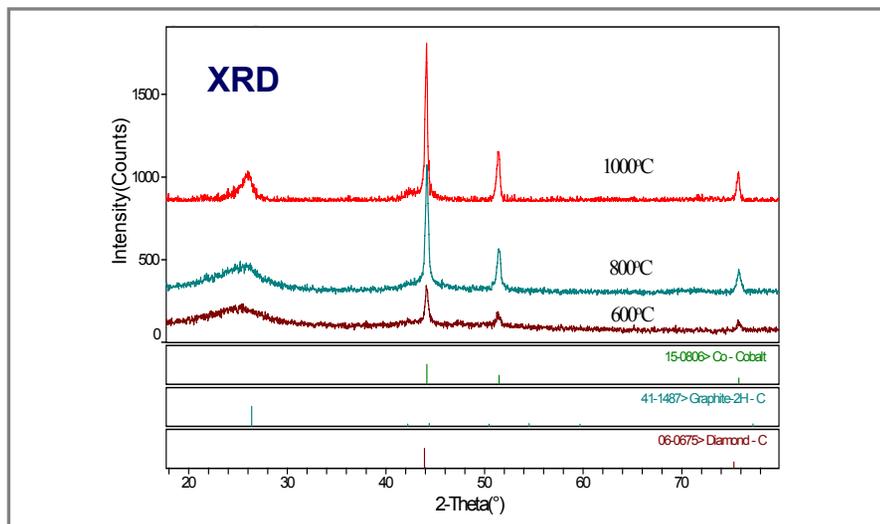


Catalyst	<i>n</i>	% H ₂ O ₂
	at 0.5 V vs. SHE	
Co-NH ₃ /C(K1)	2.9	50.3
Co-NH ₃ /C(K2)	3.1	42.3
Co-ND1/C(K1)	3.5	23.4
Co-ND1/C(K2)	3.8	13.0
Co-ND3/C(K1)	3.9	7.0
Co-Te-NH ₃ /C(K1)	3.9	5.1

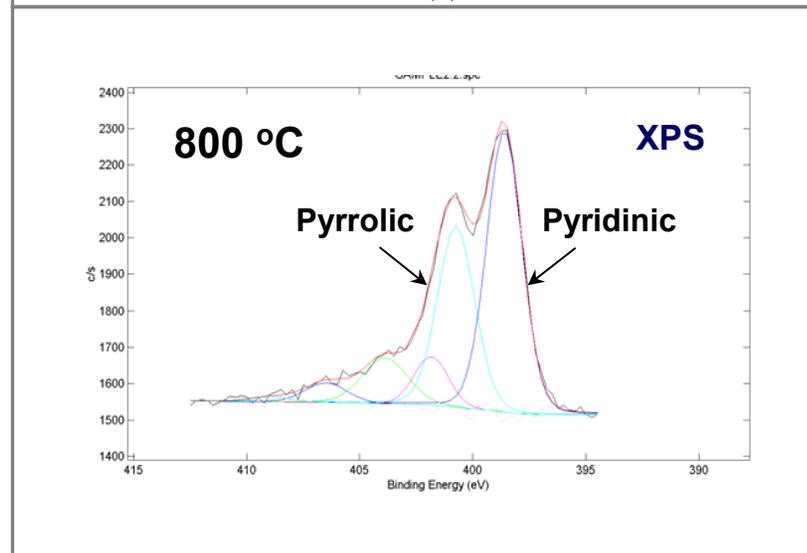
- **HIGHLIGHT:** Co based catalysts show comparable performance with Pt/C catalysts under RRDE test conditions:
 - Onset potential for O₂ reduction – 0.85 V vs. SHE
 - Four electron pathway for ORR



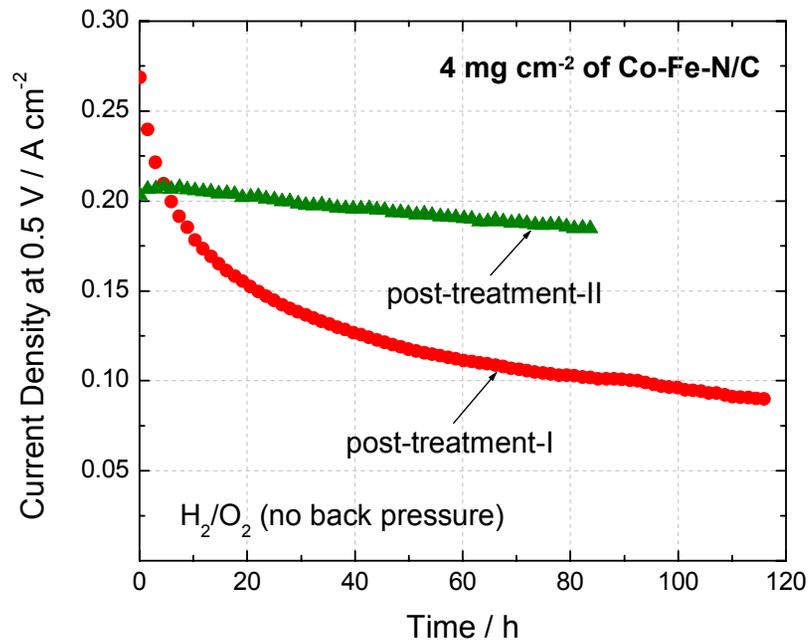
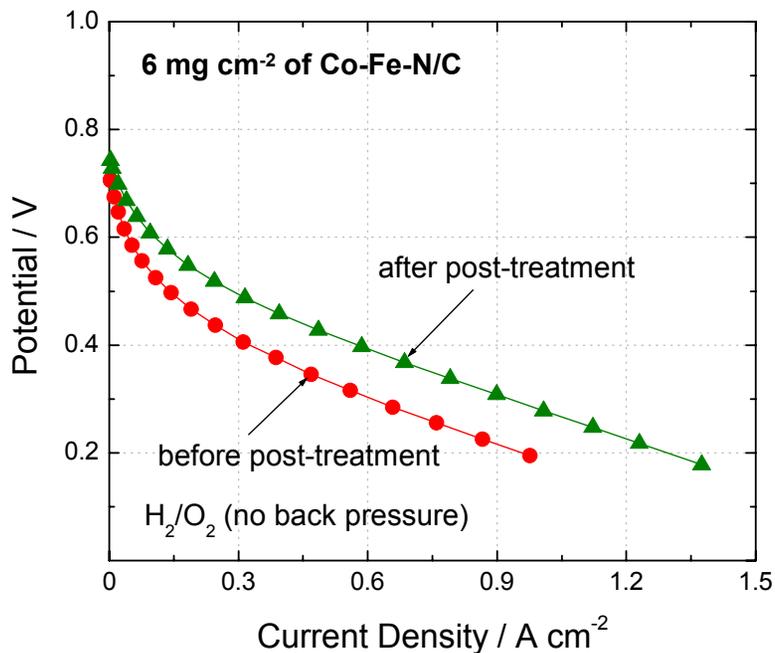
Co-Based Catalysts



- **HIGHLIGHT:** Pyrolysis temperature was optimized to be 800 °C (data not shown).
- **XRD:** Concentration of metallic Co increases with increase in heat-treatment temperature. The carbon tends to become more graphitic.
- **EXAFS:** At 600 °C and beyond only Co-Co interaction is observed.
- **XPS:** A specific ratio of pyridinic and pyrrolic nitrogen groups at 800 °C maximizes the activity of the catalysts.



Co-Based Catalysts



- **Anode:** 2 mg cm⁻² of E-TEK 20% Pt/C (0.4 mg cm⁻² Pt)
- **Cathode:** 4 or 6 mg cm⁻² of Co-Fe-N/C
- **Membrane:** Nafion™ 112
- **Operating temperature:** 77 °C (H₂); 75 °C (O₂); 75 °C (cell)

- **HIGHLIGHT:** The chemical post-treatment significantly increases the fuel cell performance and stability.



Lessons Learned from the Initial Work

FROM CHEMISTRY & ELECTROCHEMISTRY THEORY:

- ❑ Porphyrin-based macrocyclic compounds can contain at most **0.2 wt% metal**.
⇒ metal-N_x site density ≈ ca. 8.6×10^{18} sites cm⁻³ ≈ 1/37th of the density for Pt
- ❑ The exchange current density for ORR on transition metals is far lower by several orders of magnitude than that on Pt.

FROM OUR EXPERIMENTAL FINDINGS:

- ❑ The nitrogen incorporation increases the catalytic activity and selectivity due to the increased Lewis basicity of carbon.
- ❑ The Co-N complex is not stable upon pyrolysis at higher temperatures than 800 °C.
- ❑ The leaching of Co from the catalyst during post chemical treatment does not cause any loss of the catalytic activity, but increases the activity, selectivity and durability.



Specific Focus on Carbon-Based Catalysts (FY 2005 - 2007)

OVERALL OBJECTIVE: To develop highly active carbon-based catalyst with:

- active reactions sites with strong Lewis basicity (π electron delocalization) to facilitate reductive O₂ adsorption
- nano-structured graphitic carbon with high stability

Carbon-based metal-free catalyst (MFC)

Optimization of active reaction sites

as a function of:

- (1) surface oxygen groups***
- (2) nitrogen content and precursor***
- (3) carbon support***
- (4) porosity and pore size distribution***
- (5) pyrolysis temperature***
- (6) non-metallic additive "X"***

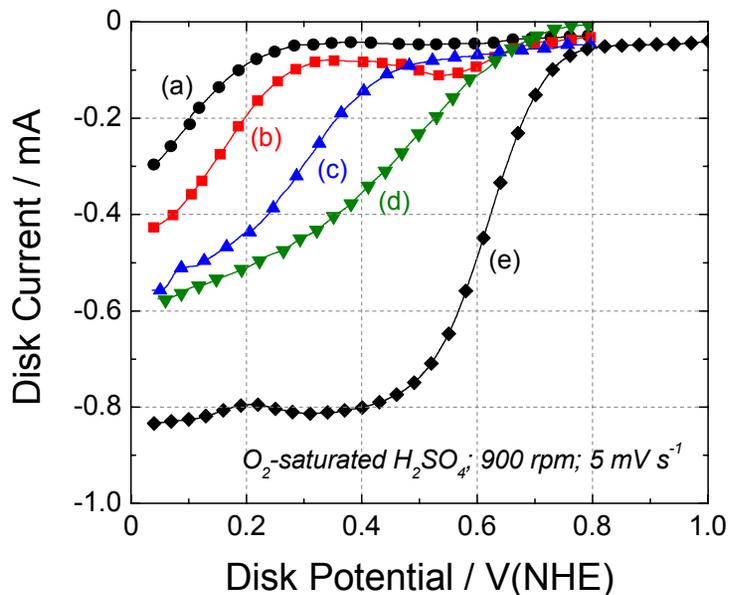
Carbon composite catalyst

The following steps were performed to develop carbon composite catalyst:

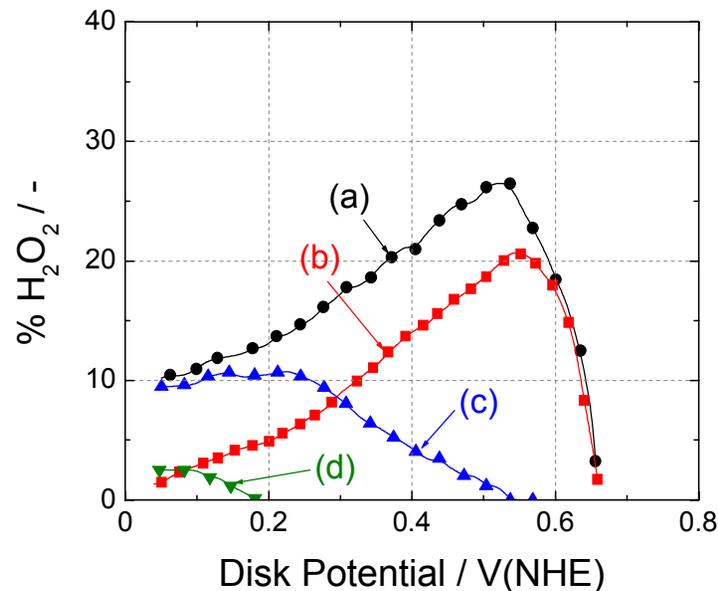
- (1) Use of metal-free catalyst as a catalyst support***
- (2) Metal-catalyzed pyrolysis to increase the number of active sites***
- (3) Chemical post-treatment***



Carbon-Based Metal-Free Catalysts



(a) as-received carbon; (b) Treatment with HNO_3 ;
 (c) Treatment with NH_3 ; (d) USC Methodology - 1;
 (e) USC Methodology - 2

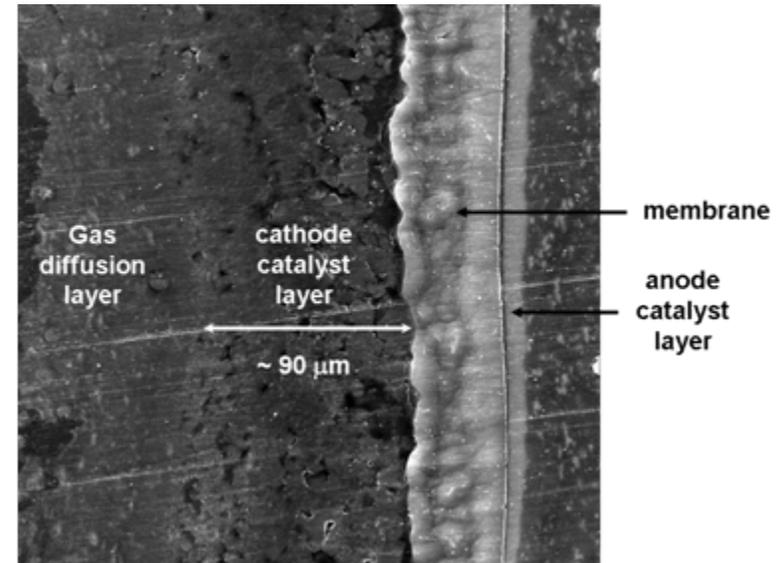
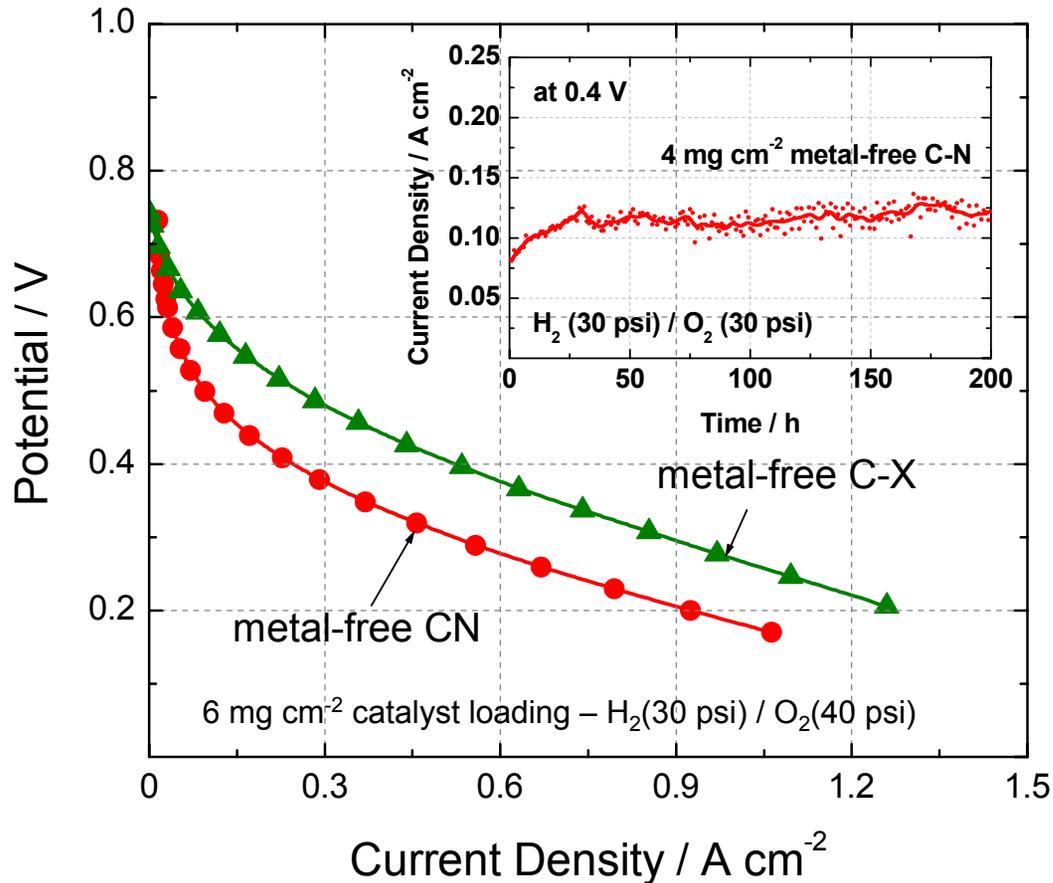


(a) MFC-1; (b) MFC-2;
 (c) MFC-3; (d) MFC-4

- HIGHLIGHT:** The USC methodology increases the onset potential for oxygen reduction by ca. 500 mV, as compared with the as-received carbon.
- The USC-developed “MFC-4” catalyzes oxygen reduction to water via four-electron transfer with no H_2O_2 production (above 0.2 V vs. NHE).



Carbon-Based Metal-Free Catalysts

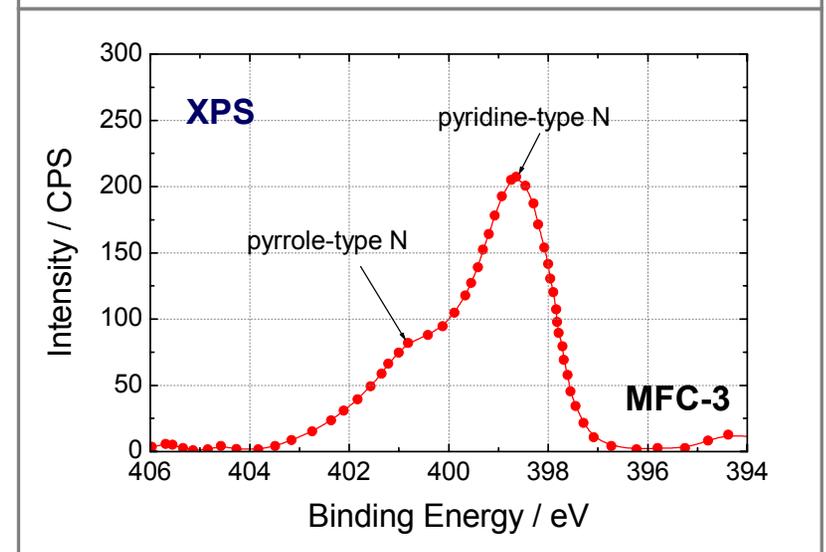
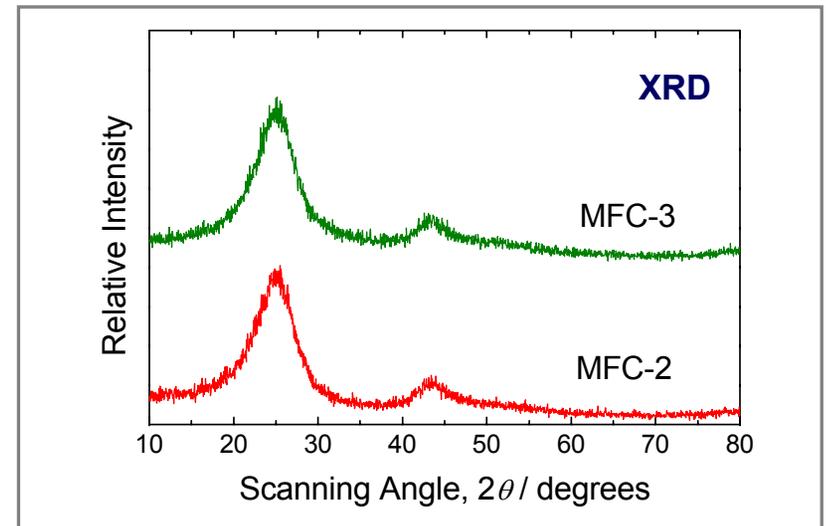
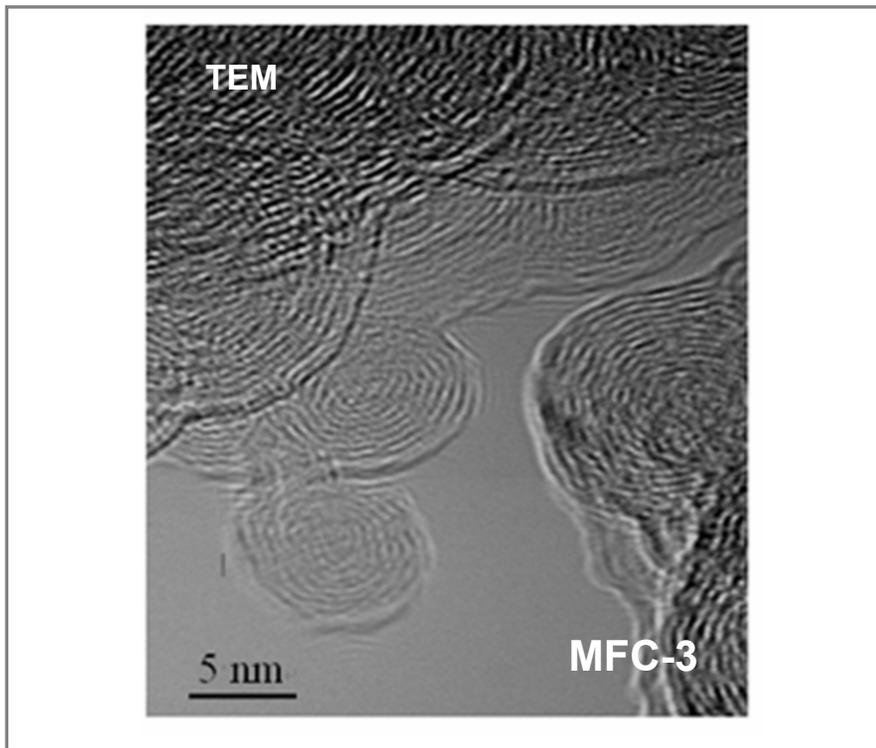


Cross-section of MEA with the metal-free C-X cathode catalyst.

- **Anode:** 2 mg cm⁻² of ETEK 20% Pt/C
- **Membrane:** Nafion™ 112
- **Operating temperature:** 77 °C (H₂); 75 °C (O₂); 75 °C (cell)



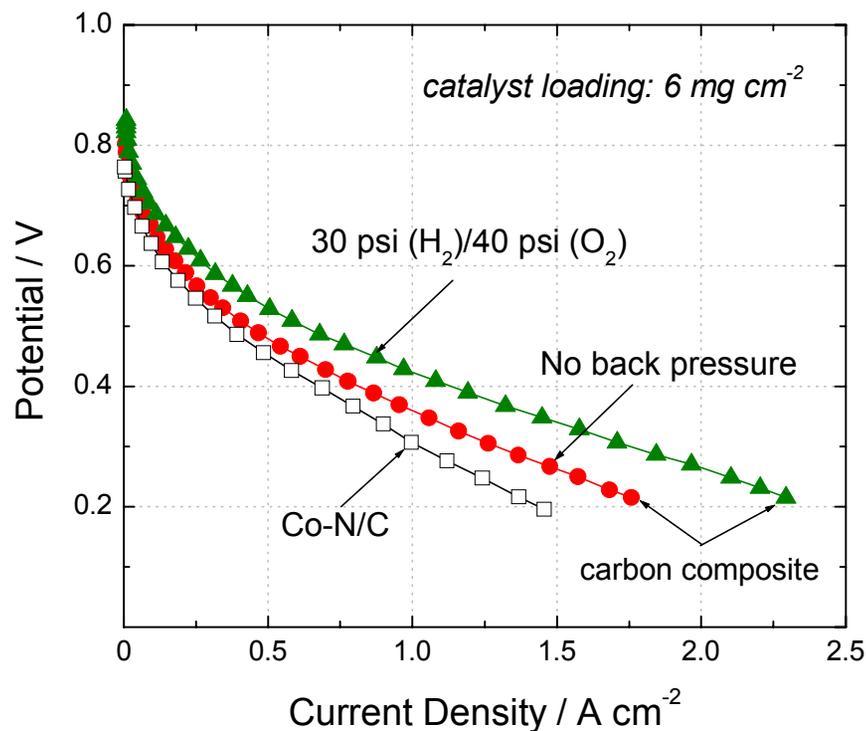
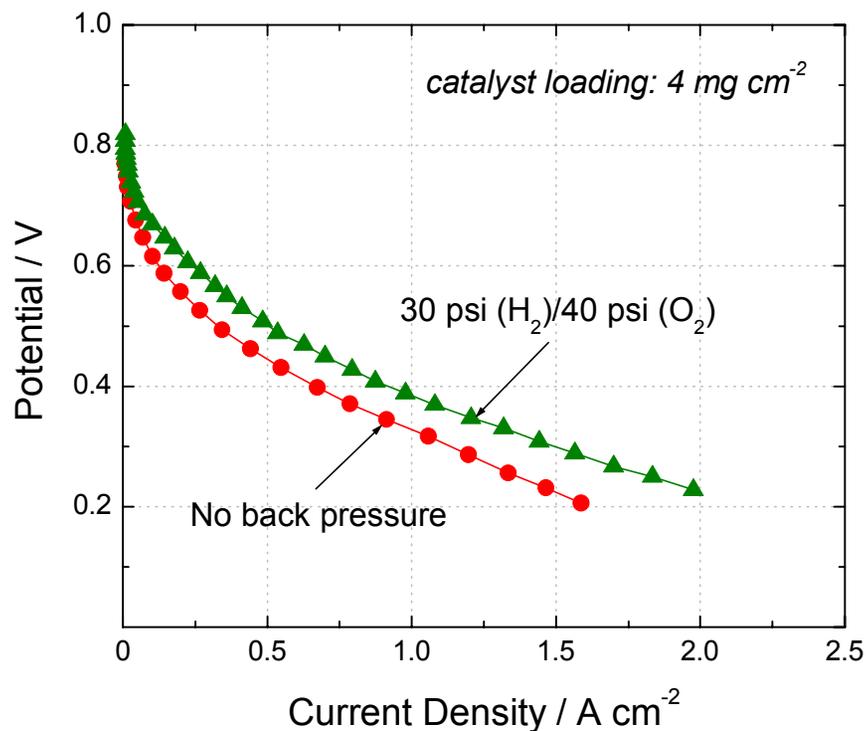
Carbon-Based Metal-Free Catalysts



- **HIGHLIGHT: TEM & XRD:** No metallic elements in the synthesized catalysts.
- **XPS:** High-temperature pyrolysis leads to the formation of pyrrole- and pyridine-type nitrogen.



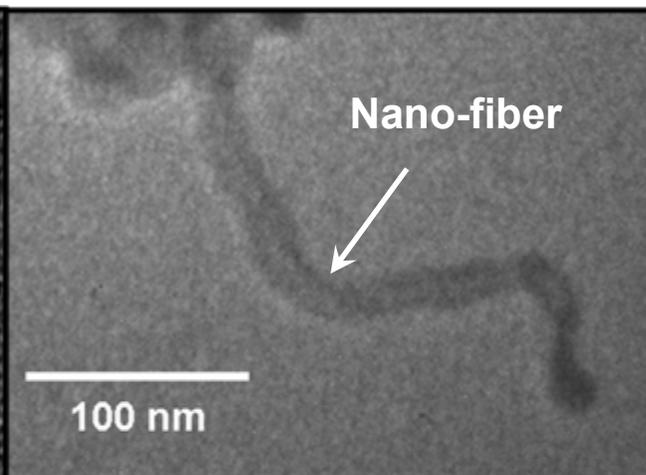
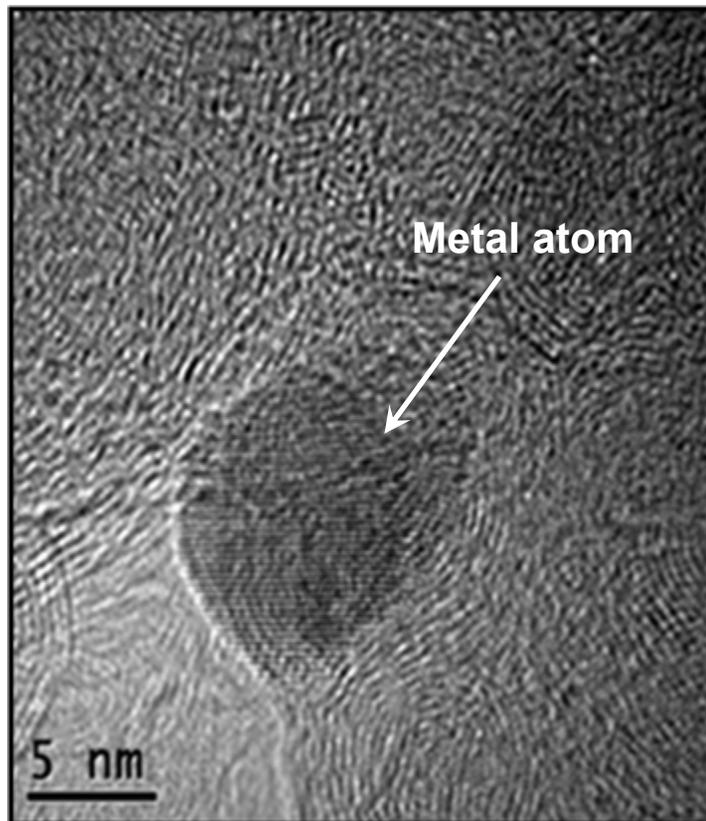
Carbon Composite Catalysts



- **Anode:** 2 mg cm⁻² of E-TEK 20% Pt/C (0.4 mg cm⁻² Pt)
- **Cathode:** 4 or 6 mg cm⁻² of carbon composite catalyst
- **Membrane:** Nafion™ 112
- **Operating temperature:** 77 °C (H₂); 75 °C (O₂); 75 °C (cell)



Carbon Composite Catalysts



Surface concentration determined by XPS

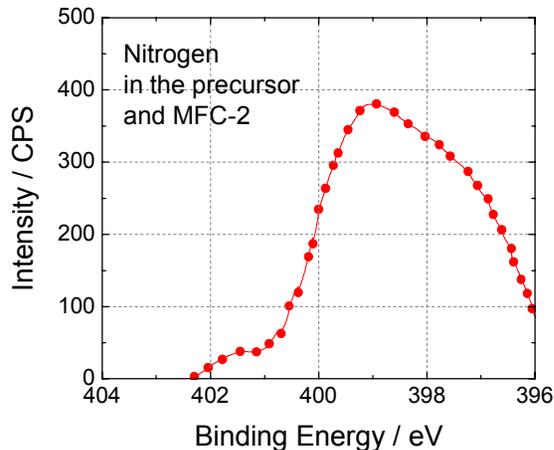
C	O	N	Co	Fe
94.86	1.26	3.88	-	-

- **HIGHLIGHT:** Metal atoms are covered with several graphitic layers.
- Nanostructured fiber of graphitic carbon was formed as a result of metal-catalyzed pyrolysis.
- No metal traces were detected on the surface of carbon composite catalyst.

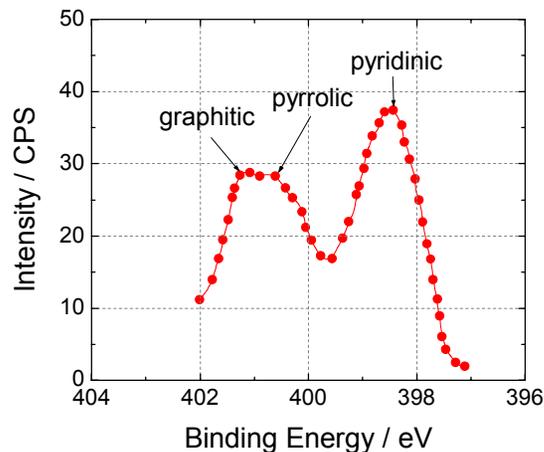


Carbon Composite Catalysts

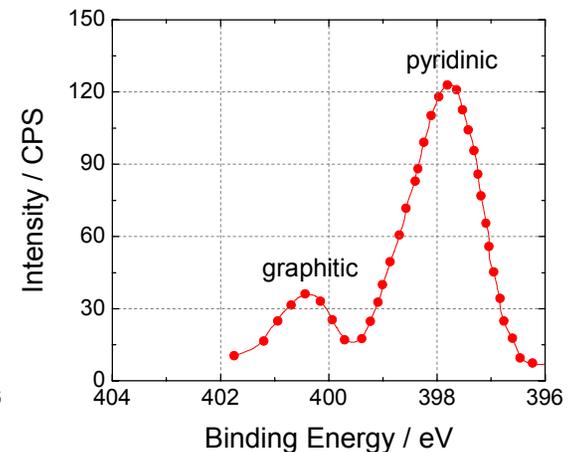
before pyrolysis



after pyrolysis



post-treatment



Potential

Current density ($A\ cm^{-2}$)

0.7 V

0

0.03 with ~15% H_2O_2

0.05 with ~1.5% H_2O_2

0.4 V

0.3 with ~ 37% H_2O_2

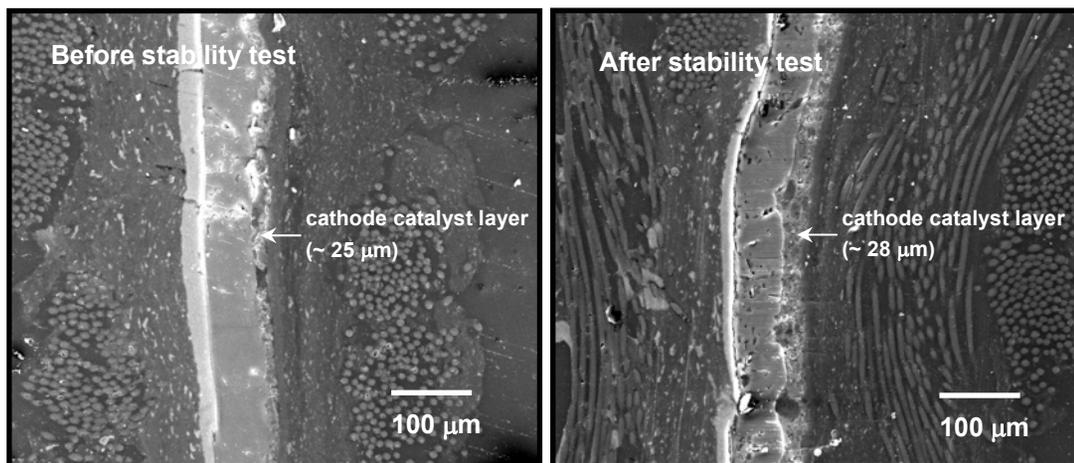
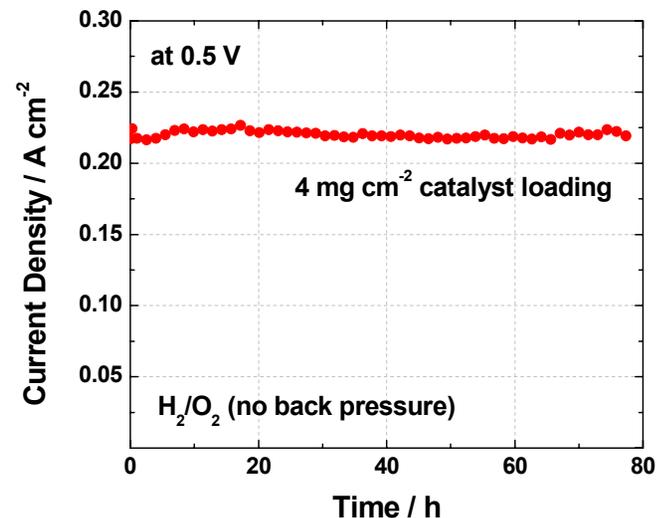
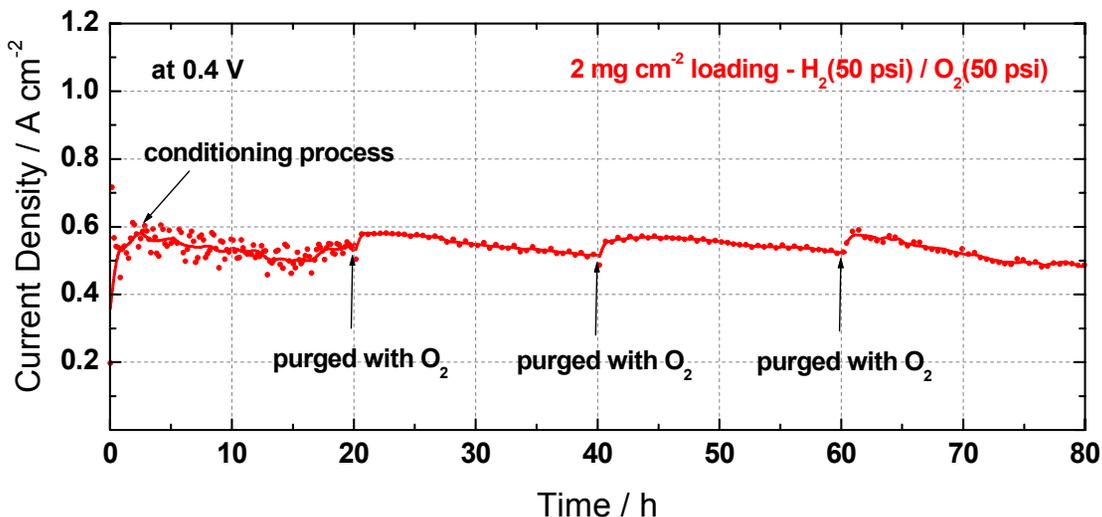
0.7 with ~ 10% H_2O_2

0.9 with ~1.5% H_2O_2

- **HIGHLIGHT:** High-temperature pyrolysis increases the Lewis basicity due to the increased concentration of pyridine-type nitrogen, and incorporates the nitrogen into graphitic structures which increases the stability.
- Post-treatment increases the concentration of pyridinic-type nitrogen while removing pyrrolic-type nitrogen.



Carbon Composite Catalysts – Durability Study



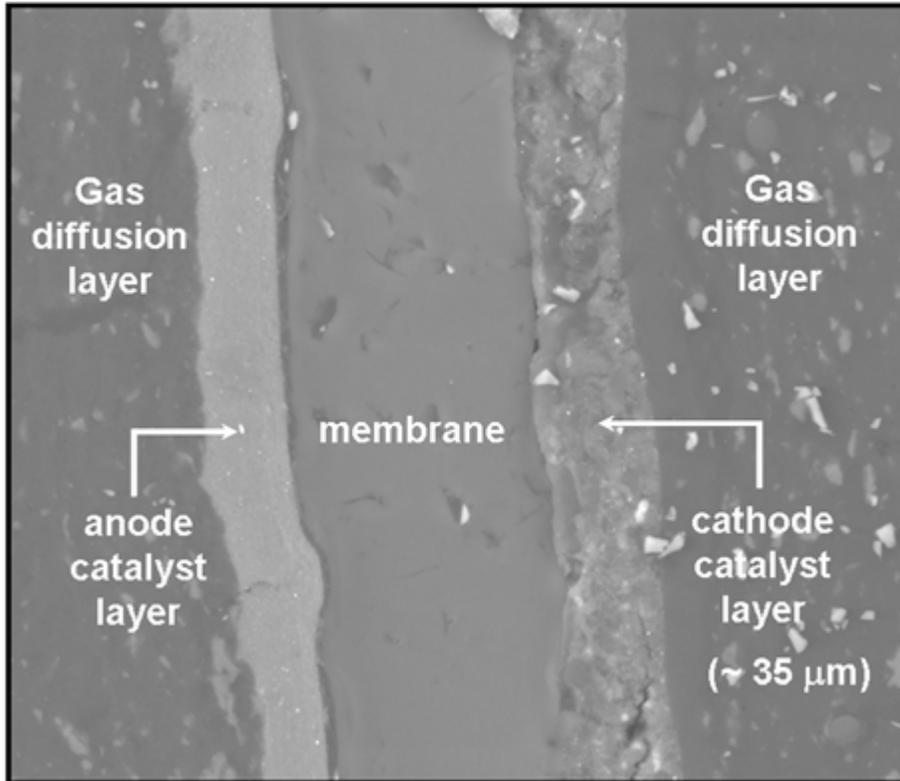
- **HIGHLIGHT:** No significant degradation of the catalyst is observed.

- Water management should be optimized.

Cross-section of MEA with the carbon composite cathode catalyst (2 mg cm⁻²) before and after stability test for 80 h



Future Work



ENGINEERING OF CATALYST LAYER:

- To improve water management by controlling hydrophobicity of the catalyst layer and by reducing the catalyst layer thickness
- To increase the fuel cell performance by optimizing the catalytic sites
- To reduce the resistance of the catalyst layer

SEM image of the cross-section of MEA with the carbon composite cathode catalyst.



Summary

- ❑ **Objective:** Develop carbon-based metal-free catalysts and carbon composite catalysts for PEMFC which perform as well as conventional Pt catalysts.
- ❑ **Approach:** Optimize the active reaction sites to increase the catalytic activity and stability using USC-developed methodology.
- ❑ **Technological Accomplishments and Progress:** Demonstrated high catalytic activity (0.82 – 0.85 V vs. SHE), selectivity (0 – 1 % H₂O₂) and stability (for 80 h) for carbon-based catalysts.
- ❑ **Collaborations:** Active partnership with Case Western Reserve University and Northeastern University. Northeastern University was unable to prepare stable Co chalcogenide catalysts.
- ❑ **Proposed future research:** Optimize MEA performance and stability with the carbon composite catalysts by improving water management.

